

# Assessment of hydrocarbon electron-impact ionization cross section measurements for magnetic fusion

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## Abstract

Partial ionization cross section experiments have been carried out recently at the University of Innsbruck for three types of hydrocarbons, i.e. acetylene, ethylene and propene. Cross section data fits are generated and compared to the compilation of earlier experimental data summarized in the online database HYDKIN [www.hydkin.de]. New data fits are brought into a suitable form to be incorporated into the database. In order to illuminate underlying dissociation mechanisms the energy dependence of branching ratios above energies of 20 – 30eV is reviewed in light of the present results.

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## I. INTRODUCTION

Since graphite is still a candidate as wall material for the high flux zones at the divertor of the fusion experiment ITER, hydrocarbon impurities will be formed due to chemical erosion [1–3]. A key ingredient for the simulation of the transport, chemistry, and radiation behaviour of these impurities are the cross sections for collision processes with electrons and protons present in the scrape-off layer (SOL) plasma [4, 5]. For that reason, the HYDKIN cross section database [6] has been set up over the last decades to cover the information on such cross sections. Much experimental cross sectional data have been compiled and a revision of many of the data used in HYDKIN has recently been carried out and presents the current state of the HYDKIN database [7]. Concerning especially (dissociative) ionization cross sections, fit curves of experimental data have been determined by making use of the following fitting expression [4, 5, 7]:

$$\sigma(E) = \frac{10^{-13}}{EE_{th}} \left[ A_1 \ln(E/E_{th}) + \sum_{j=2}^N A_j \left( 1 - \frac{E_{th}}{E} \right)^{j-1} \right], \quad (1)$$

where  $\sigma(E)$  denotes the cross section in units of  $cm^2$ ,  $E$  is the collision energy expressed in  $eV$ , and  $A_j, j \in \{2, \dots, N\}$  are fitting parameters.  $N$  has been set to values such that the r.m.s. of the fit is smaller than 2–3%, i.e.  $N = 6$  in most cases. The factor  $10^{-13}$  has been singled out from the fitting parameters in order to make them more handy for both the user and the used fit software.  $E_{th}$  is the appearance potential (also expressed in  $eV$ ), depending on the considered process. In addition, cross sections have been generated for processes, for which no experimental data have been available, by making use of well-based (auxiliary) assumptions, like energy invariance of branching ratios (see Sec. IIID), and certain well established cross section scaling rules [4, 5, 7].

In 2006 and 2009, respectively, partial electron impact ionization cross section experiments have been carried out at the University of Innsbruck for three types of hydrocarbons, i.e. acetylene [8], ethylene [9] and propene [10]. In this work the results of these measurements are first used to generate cross section fits for the processes covered by these experiments to be subsequently compared to the compilation of experimental data available in HYDKIN for acetylene [11], ethylene [12] and propene [13, 14]. It should be kept in mind that when the discussion appears to be about agreement of new cross section fits with the HYDKIN database, this is just short for a comparison of present experimental data to earlier experi-

mental data on which the HYDKIN database is based.

After summarizing shortly the methodology of fitting the recent experimental data as well as the sources for ionization and appearance potentials in Sec. II, the new cross section fits are presented and compared to already existing cross section expressions provided by HYDKIN in the subsequent Secs. III A-III C. In Sec. III D the energy dependence of branching ratios for large energies is reviewed in light of the recent data. Finally, in Sec. IV, a conclusion is summarized.

## II. METHODOLOGY

In order to generate cross section fits considering partial electron impact ionization cross sectional data, expression 1 has been used to determine the fitting coefficients  $A_j$  with  $N = 6$  in most cases. It has been shown elsewhere that cross sections given by Eq. (1) provide a proper physical energy dependence in the threshold and high energy regions with the fitting coefficients  $A_j$  fulfilling certain conditions [7]. These conditions are met by the coefficients for the processes presented in Secs. III A-III C. In case of electron impact cross sections the collision energy  $E$  can be set approximately equal to the electron impact energy with high accuracy due to the small mass of the electron compared the molecular masses of the molecules in consideration. The value of  $E_{th}$  is given by the ionization potential in case of ordinary ionization cross sections, and by the appearance potential in case of dissociative ionization processes, where the (experimental) appearance energy is defined as the experimentally accessible minimum energy value for the appearance of ionic fragments [15]. The numerical values for both the ionization and the appearance potentials for the processes discussed in this work have mainly been adopted from Refs. [8, 16–18] concerning acetylene, from Refs. [10, 19] concerning ethylene, and from the data compilation provided by NIST chemistry webbook [20] concerning propene as well as some specific dissociation channels concerning the former two hydrocarbons. In specific cases no experimental values for the threshold energy  $E_{th}$  have been available. The choice of  $E_{th}$  concerning such cases will be discussed when discussing the cross section fits for the corresponding processes in Secs. III A-III C.

### III. RESULTS

#### A. Acetylene

Ionization cross section fits for the following electron-impact ionization processes of acetylene, revealed by the measurements of Feil et al. [8], have been generated:

$$e + C_2H_2 \rightarrow C_2H_2^+ + 2e, \quad (2a)$$

$$\rightarrow C_2H^+ + H + 2e, \quad (2b)$$

$$\rightarrow C_2^+ + \dots, \quad (2c)$$

$$\rightarrow CH^+ + \dots, \quad (2d)$$

$$\rightarrow C^+ + \dots, \quad (2e)$$

$$\rightarrow CH_2^+ + C^+ + 3e, \quad (2f)$$

$$\rightarrow C_2H_2^{2+} + 3e, \quad (2g)$$

where the dots designate the sum of all possible dissociation sub channels. Since it is only possible to distinguish product ions with a mass spectrometer with respect to their mass to charge ratio, in a first step a cross section for the sum of processes (2e,2g) has been measured by Feil et al. [8], because both  $C_2H_2^{2+}$  and  $CH^+$  have mass to charge ratio of 13 Thompson. In a second step cross sections differential with respect to ion kinetic energy have been determined. These yield cross sections for fragment ions with low initial kinetic energy ( $< 0.5eV$ ) and high initial kinetic energy ( $0.55 - 10eV$ ). As ionization of  $C_2H_2$  resulting in  $C_2H_2^{2+}$  does not change the momentum of the product ion, the low kinetic energy part has been assigned to the formation of  $C_2H_2^{2+}$ , whereas the high energy part has been assigned to the production of  $CH^+$  fragments [8]. In addition, also the threshold of the low kinetic energy cross section has been observed to be about  $36eV$  which corresponds nicely with the ionization energy of  $^{13}C^{12}CH_2^{2+}$ , which has been determined separately [8].

The fitting coefficients  $A_j$ , according to Eq. (1) as well as the threshold energies  $E_{th}$  for the cross section fits for the processes listed above are given in table I.

The results of the experiments on acetylene contain new data of one process which has not been included into HYDKIN so far, which is process 2f. However, the magnitude of that cross section is small ( $\sim 2.7 \cdot 10^{-18}cm^2$  at maximum). The other new cross section fits have been compared to those available in the HYDKIN database by calculating the normalized

TABLE I. Values of fitting parameters  $E_{th}$  (with references in squared brackets) and  $A_i$  in Eq. (1) for partial ionization cross sections of acetylene.

Reaction $e + C_2H_2 \rightarrow$	$E_{th}$	$A_i, i = 1 - 3$		
		$A_i, i = 4 - 6$		
$C_2H_2^+ + 2e$	1.14000E+01 [6, 20]	3.73243E+00	-3.73243E+00	-8.01475E-01
		3.15344E+00	-1.00779E+01	7.28853E+00
$C_2H^+ + H + 2e$	1.73000E+01 [18]	7.96959E-02	-7.96959E-02	3.96012E+00
		-7.24695E+00	3.70496E+00	2.81512E+00
$C_2^+$ (total)	1.84400E+01 [16]	2.04011E-03	-2.04011E-03	2.14350E-03
		1.62930E+00	-2.41224E+00	1.76375E+00
$CH_2^+ + C^+ + 3e$	2.80000E+01 [8]	1.10130E-09	-1.10130E-09	4.87997E-01
		-1.45604E+00	1.84000E+00	-6.60842E-01
$CH^+$ (total)	2.08500E+01 [17]	9.40467E-13	-9.36864E-13	4.50043E-10
		1.05143E+00	-4.68811E-01	7.14727E-01
$C^+$ (total)	2.12000E+01 [16]	2.90265E-18	-2.90265E-18	6.15814E-02
		-2.10614E-01	1.83046E+00	-1.23394E+00
$C_2H_2^{2+} + 3e$	3.62000E+01 [8]	1.66952E-01	-1.37602E-01	-2.43008E-02
		-1.39968E+00	9.24969E+00	-8.49667E+00

root mean square deviation,  $d$ , for the entire ( $E_{th} < E < 1000eV$ ), low ( $E_{th} < E < 100eV$ ) and high energy range ( $100eV < E < 1000eV$ ). In addition, the deviation of the maximum values of the cross section fits relative to the corresponding HYDKIN curves,  $\Delta\sigma_{max} = (\sigma_{new}^{max} - \sigma_{hyd}^{max})/\sigma_{hyd}^{max}$ , as well as the energy shift of the maxima,  $\Delta E_{max} = E_{max,new} - E_{max,hyd}$ , i.e. the difference of the energy locations of the maxima of two corresponding cross section fits, have been calculated. The values of the mean deviation as well as the deviation of the maxima and the maximum shift for each pair of corresponding curves are given in table II.

TABLE II. Accordance of present cross section fits with those based on earlier data compiled by HYDKIN for the case of acetylene. Dissociation channels are indicated by product ions.

$C_2H_2 \rightarrow$	$C_2H_2^+$	$C_2H^+$	$C_2^+$	$CH^+$	$C^+$	$C_2H_2^{2+}$
$d$ in % for $E_{th} < E < 1keV$	3.3	11.0	13.4	19.9	49.5	101
$d$ in % for $E_{th} < E < 100eV$	6.3	30.0	13.1	36.3	27.8	270
$d$ in % for $100eV < E < 1keV$	3.0	7.6	13.4	18.0	50.9	80
$\Delta\sigma_{max}$ in %	-3.6	22.4	3.6	-33.2	-33.8	206
$\Delta E_{max}$ in eV	14.5	-0.8	5.0	12.3	-17.8	-48.2

The accordance of the curves is rather good, i.e. the deviation is less than the estimated experimental error of about 15%, for processes (2a,2c) and the high energy range of process (2b). For the rest of new cross section fits the deviations lie in a range of 18 – 51%, with

exception of the fit for process (2g) which shows a completely different energy dependence than the corresponding one provided by HYDKIN.

Also the direction of the deviation, i.e. if the new cross section fit is larger or smaller in magnitude than the HYDKIN one, is not unambiguous. In case of process (2b) the cross section is larger than the one provided by HYDKIN, where in case of processes (2e,2f) it is smaller.

Most interesting is the energy behaviour of the cross section for process (2g) which differs in many aspects from the corresponding one provided by HYDKIN. The new data fit for this process and the result from HYDKIN is shown in Fig. 1. Comparing the magnitude of both cross section data fits a difference of 200% can be observed near the maxima. Moreover, the maximum of the new data fit is located at about 50eV lower energy, leading thereby to a much steeper increase of the cross section right after the energy threshold. The most unexpected feature of process (2g) is its steep decrease after the maximum, affecting also the assumption of approximately constant branching ratios, which will be discussed in more detail in Sec. IIID. However, it might be interesting to note that the new cross section fit for the sum of processes (2e,2g) accords to that one given by HYDKIN rather well within 20%, indicating thereby that the measurements of Feil et al. are in accordance with earlier cross section experiments for the  $m/z = 13$  Thompson dissociation channel, but the contribution of the two underlying processes determined by using cross sections differential to ion kinetic energy is different than expected.

## B. Ethylene

Ionization cross section data fits for the following electron-impact processes of ethylene, obtained by the measurements of Endstrasser et al. [9], have been generated by making use

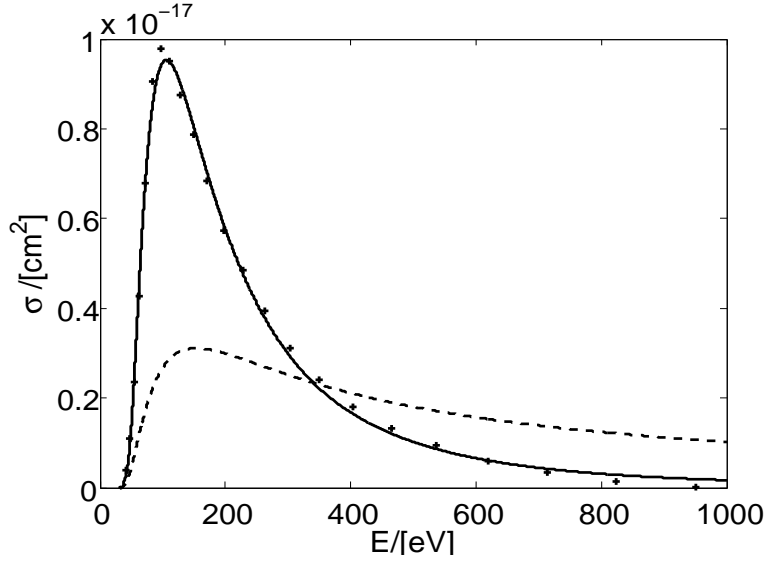


FIG. 1. Graphical comparison between new (solid line) and HYDKIN (dashed line) cross section fit for the process  $e + C_2H_2 \rightarrow C_2H_2^{2+} + 3e$ . The experimental data from Ref. [8] is shown too (crosses).

of Eq. 1:

$$e + C_2H_4 \rightarrow C_2H_4^+ + 2e, \quad (3a)$$

$$\rightarrow C_2H_3^+ + H + 2e, \quad (3b)$$

$$\rightarrow C_2H_2^+ + \dots, \quad (3c)$$

$$\rightarrow C_2H^+ + \dots, \quad (3d)$$

$$\rightarrow C_2^+ + \dots, \quad (3e)$$

$$\rightarrow CH_3^+ + \dots, \quad (3f)$$

$$\rightarrow CH_2^+ + F + 2e. \quad (3g)$$

$$\rightarrow CH_2^+ + F^+ + 3e. \quad (3h)$$

$$\rightarrow CH^+ + \dots, \quad (3i)$$

$$\rightarrow C^+ + \dots, \quad (3j)$$

$$\rightarrow H_2^+ + \dots, \quad (3k)$$

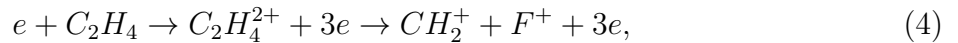
$$\rightarrow H^+ + \dots, \quad (3l)$$

$$\rightarrow C_2H_3^{2+} + H + 3e, \quad (3m)$$

$$\rightarrow C_2H^{2+} + \dots, \quad (3n)$$

where  $F$  denotes some unspecified neutral fragments and  $F^+$  some unspecified fragment ions, and the dots again designate the sum of all possible dissociation sub channels. The fitting coefficients (together with threshold energies) for the cross section fits according to the processes listed above are given in table III. The threshold energies for processes (3m,3n) have been estimated during the fitting procedure, because no appropriate experimental values have been found.

The cross sections for processes (3g-3i) have been determined after subtracting the contributions from the ionization channels containing  $C_2H_4^{2+}$ ,  $^{13}CCH_3^{2+}$  with  $m/z = 14$  for the  $CH_2^+$  product ion channels and the contributions from the  $^{13}C^+$ ,  $^{13}CCH^{2+}$ ,  $C_2H_2^{2+}$  channels with  $m/z = 13$  for the  $CH^+$  product ion channel, since it is only possible to distinguish product ions with respect to their mass to charge ratio with a mass spectrometer. In the former case, the contribution has been estimated to be about 12% of the total  $m/z = 14$  product ion channel, and in the latter case to be about 11% of the total  $m/z = 13$  product ion channel, see also Ref. [9]. A distinction between processes (3g,3h) which contain the same fragment ion  $CH_2^+$  has been possible by making use of the corresponding cross sections differential to initial ion kinetic energy given in Ref. [9]. Therein the quasithermal part ( $< 0.5\text{eV}$ ) of the cross section has been assigned to direct dissociative ionization, i.e. process (3g), and the high energy and dominating part of the cross section to process (3h). The latter is expected to be most likely produced via Coulomb explosion of the doubly charged parent ion [9]:



where  $F^+$  denotes a set of fragments with one of them being ionized, e.g.  $F^+ = C^+ + H_2$ . For process (3k) it has been necessary to increase the number of fitting coefficients to  $N = 8$  to obtain a physically well behaving fit. However, the near threshold behaviour of this cross section fit is untypical as well as the cross section fit of process (3l), see figure 2. This might be an indication that these cross sections are superpositions of two distinct cross sections for different processes with completely different threshold energies. Possible processes are direct dissociative ionization with fragment ion  $H_2^+$  or  $H^+$ , respectively, and some Coulomb explosion of an intermediate doubly charged ion with a much enhanced energy threshold in the range of  $30 - 50\text{eV}$ .

As for the previously discussed molecule acetylene, also for ethylene the cross section fits for (dissociative) ionization have been compared to earlier data compiled by HYDKIN. The



TABLE III. Values of fitting parameters  $E_{th}$  (with references in squared brackets if data have been appropriate and available) and  $A_i$  in Eq. (1) for partial ionization cross sections of ethylene. The cross sections marked with an asterisk have to be corrected for a contribution of about 40% of the  $F$  cross section to the  $F^+$  cross section [21].

Reaction $e + C_2H_4 \rightarrow$	$E_{th}$ in eV	$A_i, i = 1 - 3$		
		$A_i, i = 4 - 6$		
$C_2H_4^+ + 2e$	1.05100E+01 [6, 20]	1.55251E+00	-1.42571E+00	3.33972E-01
		1.92836E-01	-3.85851E+00	2.77265E+00
$C_2H_3^+ + H + 2e$	1.30900E+01 [6, 20]	2.20951E+00	-2.13713E+00	-3.31816E-01
		8.37883E-02	-7.02670E-01	-2.15846E-01
$C_2H_2^+(\text{total})$	1.32300E+01 [6, 20]	1.42515E+00	-1.40155E+00	-3.05908E-02
		1.19451E+00	-3.93545E+00	3.05752E+00
$C_2H^+(\text{total})$	1.90600E+01 [6]	2.73180E-01	-2.73180E-01	-9.10600E-02
		1.46495E-01	2.95188E+00	-2.77248E+00
$C_2^+(\text{total})$	2.45000E+01 [20]	2.64453E-10	-2.64453E-10	1.20273E-01
		3.35800E-01	5.22613E-01	-5.03272E-01
$CH_3^+(\text{total})$	1.73400E+01 [9]	1.56138E-02	-1.39287E-02	-3.51951E-03
		9.73948E-02	-1.94039E-01	1.07633E-01
$CH_2^+ + F + 2e(\text{total})^*$	1.88400E+01 [9]	1.05603E-01	-7.50799E-02	-4.67817E-03
		6.93006E-01	-2.02644E+00	1.27088E+00
$CH_2^+ + F^+ + 3e(\text{total})^*$	1.88400E+01 [9]	1.10167E-01	-9.33446E-02	-1.98998E-02
		-2.47066E-01	1.67241E+00	-8.94238E-01
$CH^+(\text{total})$	2.38700E+01 [19]	5.89932E-10	-5.89932E-10	1.73032E-01
		-1.67939E-01	1.74778E+00	-1.22661E+00
$C^+(\text{total})$	2.70000E+01 [19]	1.33872E-09	6.79653E-03	4.20114E-01
		-1.21662E+00	3.42678E+00	-2.06732E+00
$H_2^+(\text{total}), N = 8$	1.73700E+01 [9]	1.33848E-09	1.51608E-02	1.51608E-02
		-6.06545E-01	3.35538E+00	-8.14998E+00
		9.59769E+00	-4.14264E+00	
$H^+(\text{total})$	1.88800E+01 [9]	8.98889E-03	-8.98889E-03	3.33852E-01
		-1.67362E+00	3.23495E+00	-1.56285E+00
$C_2H_3^{2+} + H + 3e$	3.50000E+01	9.16389E-10	9.25783E-03	1.13076E-01
		4.85152E-01	-8.08171E-01	3.48044E-01
$C_2H^{2+}(\text{total})$	5.00000E+01	2.71243E-12	-1.86236E-12	8.41921E-03
		-3.70929E-03	-7.72609E-03	5.14723E-03

values for  $d$ ,  $\Delta\sigma_{max}$  and  $\Delta E_{max}$  are given in table IV.

The comparison of the remaining set of new cross section data fits for ethylene with counterparts compiled by HYDKIN has shown much more significant deviations as for the case acetylene. Only the cross section fits for processes (3b,3c) accord to their counterparts

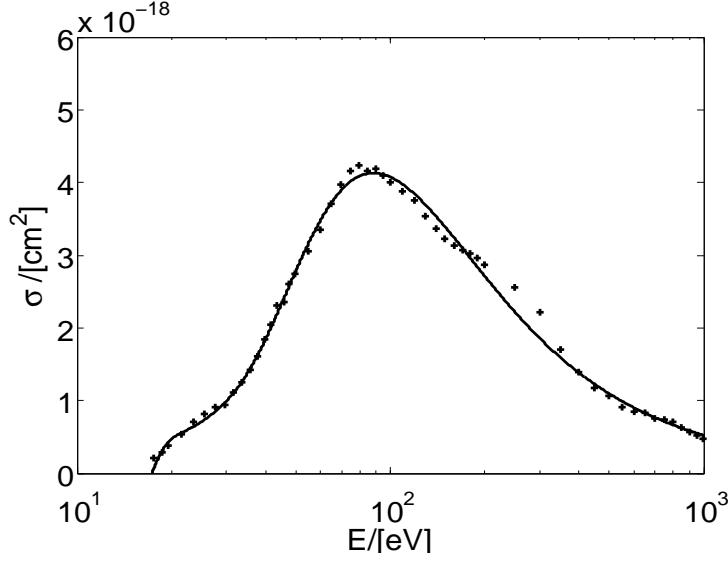


FIG. 2. Cross section fit (line) for the process  $e + C_2H_4 \rightarrow H_2^+ + \dots$ . The experimental data [9] is shown too (crosses).

TABLE IV. Accordance of present cross section fits with those provided by HYDKIN for the case of ethylene. Dissociation channels are indicated by product ions (i.e. no distinction between different dissociation subchannels wrt to neutral fragmentation; if the HYDKIN cross section belongs to a specific dissociation subchannel, the neutral fragments are given in parenthesis).

$C_2H_4 \rightarrow$	$C_2H_4^+$	$C_2H_3^+$	$C_2H_2^+$	$C_2H^+(H_2, H)$	$C_2^+(2H_2)$
$d$ in % for $E_{th} < E < 1keV$	38.3	14.7	18.0	43.2	56.8
$d$ in % for $E_{th} < E < 100eV$	27.4	42.4	47.3	100.6	90.5
$d$ in % for $100eV < E < 1keV$	39.2	8.7	12.4	34.3	53.3
$\Delta\sigma_{max}$ in %	-29.0	-3.8	-13.0	-2.3	87.3
$\Delta E_{max}$ in eV	-26.0	-9.6	-2.2	-44.2	-11.7
$C_2H_4 \rightarrow$	$CH_3^+(CH)$	$CH_2^+(CH_2)$	$CH^+(CH_3)$	$C^+$	
$d$ in % for $E_{th} < E < 1keV$	88.3	51.4	138.4	286.7	
$d$ in % for $E_{th} < E < 100eV$	85.8	61.3	183.5	313.3	
$d$ in % for $100eV < E < 1keV$	88.5	50.6	134.3	284.5	
$\Delta\sigma_{max}$ in %	-89.1	-47.7	191.1	358.0	
$\Delta E_{max}$ in eV	-38.9	-52.4	-9.6	-2.5	

provided by HYDKIN in the high energy range  $100eV < E < 1keV$  within the estimated experimental error of about 15%. The deviations at low energies range from  $\sim 30\%$  up to  $\sim 350\%$ , with exception of the two above mentioned processes not quite different from the range of the deviations at high energies. One might argue that the cross section fits provided by HYDKIN are only given for distinct dissociation channels and a comparison to

total ones (with respect to neutral fragmentation) neglects the contribution of other possible channels, but since most of the present (total) cross sections are actually smaller than the (partial) ones from HYDKIN this cannot be a sufficient explanation for all the deviations. However, most of the differences are still within 100%, with exception of processes (3i,3j), which are about a factor of 3 and 4, respectively, larger compared to the HYDKIN curves. The magnitude of these processes is larger than their counterparts in HYDKIN. This is also the case for process (3e), which is about a factor of  $\sim 1.5 - 2$  larger than its counterpart in HYDKIN. Among these three processes no other process with that property has been found. Possible reasons for the large deviations in contrast to the former case of acetylene could be due to the fact that the cross sections provided by HYDKIN for ethylene are based on experimental data only at two energies (75eV and 3.5MeV) [4].

It might also be interesting to note that the present cross sections maxima are all shifted to lower energies compared to HYDKIN, indicating thereby a steeper increase right beyond the energy threshold. These shifts range from very small values of about 2eV up to  $\sim 50$ eV. Since cross section fits for processes (3h,3k-3n) have so far not been available in HYDKIN they do not occur in table IV. It is noted here that these cross sections are rather small compared to the dominating ones, as is the case for process (2d) occurring in the catabolism of acetylene.

### C. Propene

Ionization cross section data fits for the following electron-impact processes of propene, obtained by the measurements of Feil et al. [10], have been generated:

$$e + C_3H_6 \rightarrow C_3H_6^+ + 2e, \quad (5a)$$

$$\rightarrow C_3H_5^+ + H + 2e, \quad (5b)$$

$$\rightarrow C_3H_4^+ + \dots, \quad (5c)$$

$$\rightarrow C_3H_3^+ + \dots, \quad (5d)$$

$$\rightarrow C_2H_3^+ + F + 2e, \quad (5e)$$

$$\rightarrow C_2H_3^+ + F^+ + 3e, \quad (5f)$$

$$\rightarrow C_2H_2^+ + F^+ + 3e, \quad (5g)$$

$$\rightarrow C_2H_2^+ + F'^+ + 3e, \quad (5h)$$

$$\rightarrow C_2H^+ + F^+ + 3e, \quad (5i)$$

$$\rightarrow C_2H^+ + F'^+ + 3e, \quad (5j)$$

$$\rightarrow CH_3^+ + F + 2e, \quad (5k)$$

$$\rightarrow CH_3^+ + F^+ + 3e, \quad (5l)$$

$$\rightarrow CH_2^+ + F + 2e, \quad (5m)$$

$$\rightarrow CH_2^+ + F^+ + 3e, \quad (5n)$$

$$\rightarrow CH^+ + F^+ + 3e, \quad (5o)$$

$$\rightarrow CH^+ + F'^+ + 3e, \quad (5p)$$

$$\rightarrow C^+ + \dots, \quad (5q)$$

where  $F$  again denotes some unspecified fragments,  $F^+$  some unspecified fragment ions,  $F'^+$  some highly excited unspecified fragment ions, and the dots have the same interpretation as in the previous sections. The final fitting coefficients are summarized in table V.

Cross section fits for the processes (5e-5p) have been obtained by analyzing the numerous cross sections differential to initial ion kinetic energy measured in Ref. [10]. Within this family of cross sections there exist many where the threshold energies appear to be too large to assign it to direct dissociative ionization. For this reason, Coulomb explosion of doubly charged intermediate ions might be a more reasonable assumption for explaining the high

TABLE V. Values of fitting parameters  $E_{th}$  (with references in squared brackets; if data have been appropriate and available) and  $A_i$  in Eq. (1) for partial ionization cross sections of propene.

Reaction $e + C_3H_6 \rightarrow$	$E_{th}$ in eV	$A_i, i = 1 - 3$		
		$A_i, i = 4 - 6$		
$C_3H_6^+ + 2e$	9.73000E+00 [6, 20]	1.76465E+00	-1.76444E+00	-7.19486E-01
		1.06644E+00	4.59632E-02	-1.79033E+00
$C_3H_5^+ + H + 2e$	1.19000E+01 [20]	4.78140E+00	-4.78140E+00	-2.27612E+00
		-2.81997E-01	6.18934E+00	-8.94871E+00
$C_3H_4^+(\text{total})$	1.19100E+01 [20]	1.17937E+00	-1.17937E+00	-3.93124E-01
		-5.00436E-01	1.82754E+00	-2.00461E+00
$C_3H_3^+(\text{total})$	1.31900E+01 [20]	2.38603E+00	-2.38311E+00	-8.85054E-02
		-4.55078E+00	1.03029E+01	-6.87145E+00
$C_2H_3^+ + F + 2e(\text{total})$	1.37000E+01 [20]	2.08093E-01	-2.08093E-01	3.85608E-02
		-1.36777E+00	3.77297E+00	-2.65960E+00
$C_2H_3^+ + F^+ + 3e(\text{total})$	3.20000E+01	1.02861E+00	-9.39380E-01	-2.53637E-01
		9.24639E-01	1.93228E+00	-3.84679E+00
$C_2H_2^+ + F^+ + 3e(\text{total})$	2.70000E+01	3.87573E-02	-1.28254E-02	1.30128E-02
		7.99346E-02	2.53853E-01	-3.39084E-01
$C_2H_2^+ + F'^+ + 3e(\text{total})$	3.80000E+01	4.18718E-01	-3.74737E-01	-9.55924E-02
		-2.30625E-01	1.90802E+00	-2.32656E+00
$C_2H^+ + F^+ + 3e(\text{total})$	3.45000E+01	3.70574E-10	-3.66193E-10	1.72848E-01
		-5.42785E-01	1.03012E+00	-6.24479E-01
$C_2H^+ + F'^+ + 3e(\text{total})$	5.00000E+01	1.38462E-01	-1.27538E-01	-1.96257E-02
		8.06484E-02	6.26341E-01	-9.10837E-01
$CH_3^+ + F + 2e(\text{total})$	1.70000E+01	2.92264E-11	5.00748E-04	3.43137E-02
		1.08047E+00	-2.72127E+00	1.72080E+00
$CH_3^+ + F^+ + 3e(\text{total})$	2.50000E+01	5.10937E-01	-5.10937E-01	-1.70312E-01
		1.08936E+00	-7.24946E-01	-6.60811E-01
$CH_2^+ + F + 2e(\text{total})$	1.70000E+01 [20]	4.61937E-02	-4.61937E-02	-1.53979E-02
		1.04334E-01	-7.55917E-02	-9.05605E-02
$CH_2^+ + F^+ + 3e(\text{total})$	2.50000E+01	4.01244E-01	-4.01244E-01	3.00150E-01
		-2.88555E+00	6.71214E+00	-4.69804E+00
$CH^+ + F^+ + 3e(\text{total})$	2.40000E+01	1.60325E-02	-1.60325E-02	-5.34418E-03
		9.37462E-02	-1.31281E-01	3.89138E-02
$CH^+ + F'^+ + 3e(\text{total})$	2.75000E+01	4.73250E-02	-4.73250E-02	5.46693E-02
		-6.65212E-01	2.21333E+00	-1.57914E+00
$C^+(\text{total})$	3.00000E+01	1.66755E-10	-1.66755E-10	3.29712E-01
		-1.68434E+00	3.39804E+00	-1.90085E+00

threshold energies. Since the measured cross sections are total ones with respect to neutral fragmentation channels, a further specification of  $F$  and  $F'$  would be highly speculative at this stage. However, it has been possible to distinguish between direct dissociative ionization and Coulomb explosion channels in the cases of processes (5e,5k-5n). For processes (5g-5j,5o,5p) the threshold energies of both dissociation channels are in range of Coulomb explosion channels, but the appropriate differential cross sections have shown a contribution of distinct fragmentation channels, which is indicated by the distinction between  $F$  and  $F'$ . With exception of process (5m) the threshold energies for processes (5f-5q) have been estimated during the fitting procedure, because no appropriate experimental values have been found. The numerical values for all threshold energies are given in Table V.

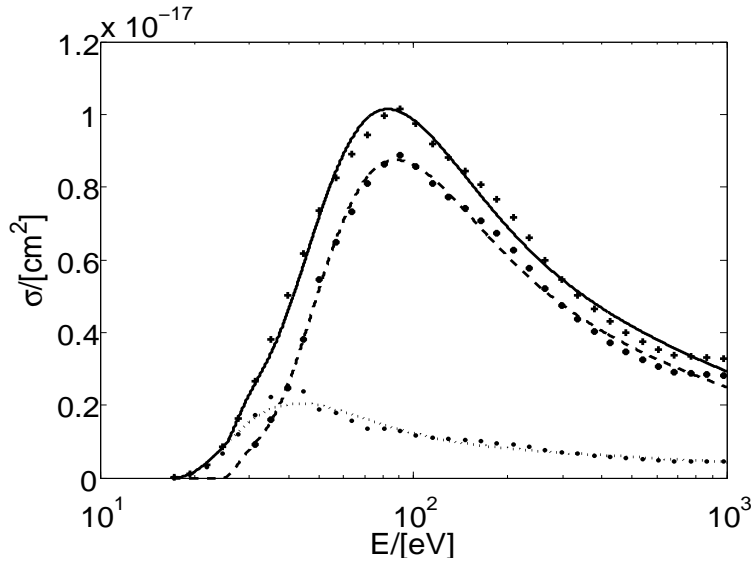


FIG. 3. Cross sections differential to ion kinetic energy: Experimental data and fits. Total cross section for the process  $e + C_3H_6 \rightarrow CH_2^+ + \dots$  (crosses and solid line), contribution from direct dissociative ionization (dots and dotted line), contribution from Coulomb explosion (asterisks and dashed line).

In figure 3 an example for the significant role of Coulomb explosion is shown: In case of ionization of  $C_3H_6$  leading to the product ion  $CH_2^+$  the Coulomb explosion channel is actually the dominating one, i.e. at higher energies (at least greater than  $\sim 50\text{eV}$ ) the probability that  $CH_2$  originates from electron-impact ionization via Coulomb explosion is much enhanced relative to direct dissociative ionization with  $CH_2^+$  being the only charged fragment.

An analogous comparison as in the previous sections has been done for seven ionization channels of propene, because all the other ionization channels (in total 10) were not included in the earlier data compiled by HYDKIN. The values for the normalized root mean square deviations  $d$  as well as the deviation of the maxima and the maximum shifts of the appropriate cross sections can be found in table VI.

TABLE VI. Accordance of present cross section fits with those provided by HYDKIN for the case of propene: The appropriate processes are indicated by product ions (i.e. no distinction between different dissociation subchannels wrt to neutrals; if the HYDKIN cross section belongs to a specific dissociation channel, the neutral fragments are given in parenthesis).

$C_3H_6 \rightarrow$	$C_3H_6^+$	$C_3H_5^+$	$C_3H_4^+(H_2)$	$C_3H_3^+(H_2, H)$
$d$ in % for $E_{th} < E < 1keV$	32.5	214.6	10.2	121.2
$d$ in % for $20eV < E < 100eV$	20.9	151.4	20.9	107.8
$d$ in % for $100eV < E < 1keV$	33.4	219.4	8.6	122.3
$\Delta\sigma_{max}$ in %	16.0	138.1	23.6	103.5
$\Delta E_{max}$ in eV	-9.4	-5.9	-2.8	-3.6
$C_3H_6 \rightarrow$	$C_2H_3^+(CH_3)$	$CH_3^+(C_2H_3)$	$CH_2^+(C_2H_4)$	
$d$ in % for $E_{th} < E < 1keV$	78.4	91.8	78.9	
$d$ in % for $20 - 30eV < E < 100eV$	74.0	87.6	70.1	
$d$ in % for $100eV < E < 1keV$	78.8	91.1	79.5	
$\Delta\sigma_{max}$ in %	-71.7	-82.1	-67.7	
$\Delta E_{max}$ in eV	-14.3	-45.2	-35.8	

With the single exception of the high energy range of process (5c), where the accordance between the new cross section fits and earlier data fits compiled by HYDKIN is rather good (8.6%), the deviations between HYDKIN curves and current results are out of the range of the estimated experimental error of 15%. The closest matching has been found for process (5a), where the deviation is  $\sim 30\%$ . In all other cases the difference in magnitude is about a factor of 2-5. For fragment ions of the type  $C_3H_y$  the recent measurements show larger values than the HYDKIN curves, where for the dissociation channels with fragment ions  $C_2H_3^+$ ,  $CH_3^+$  and  $CH_2^+$  the magnitude of the cross section is significantly smaller. As it has already been mentioned in the case of acetylene, these deviations would be smaller if no distinction between direct dissociative ionization and fragmentation due to Coulomb explosion was possible. Then, the sum of these different processes would be assigned to direct dissociative ionization. One can therefore conclude that the process of Coulomb explosion has a more important role than expected, especially for higher hydrocarbons. This statement is also confirmed by the numerous processes listed in the previous sections

that have been allocated to such processes due to their high energy thresholds. However, this effect of doubly charged intermediate ions makes the situation more complex concerning the assignment of cross sections to distinct fragmentation channels.

As a secondary remark it is noted that as in the case of ethylene, it has been observed that all of the cross sections maxima are shifted to lower energies compared to HYDKIN cross sections, and indicate therefore again a steeper increase right beyond the threshold.

#### D. Branching ratios

An ingredient for the assembly of the cross section database HYDKIN has been the assumption of (approximately) energy invariant branching ratios for multichannel processes in the energy region above 20–30eV [4]. For (dissociative) ionization processes going through a dipole allowed transition the energy invariance is based on the Born-Bethe behaviour of the cross section for large energies. Only in those cases when (dissociative) ionization proceeds by a different (non-dipole allowed) transition, e.g. a Coulomb explosion, then the typical  $\ln(cE)/E$  behaviour at high energies cannot be taken. An investigation of the energy dependence of the branching ratios based on the recent experimental data could thus illuminate the underlying dissociation mechanisms. The branching ratios  $R_j(E)$  are defined, see Ref. [4], to

$$R_{C_{x'}H_{y'}^q}(E) = \frac{\sigma_{C_{x'}H_{y'}^+}^{part}(E)}{\sigma_{C_xH_y}^{tot}(E)}, \quad (6)$$

where the  $j$ -th ionization channel is indicated by the product ion  $C_{x'}H_{y'}^q$ ,  $\sigma_{C_xH_y}^{tot}(E)$  denotes the total ionization cross section for the parent molecule  $C_xH_y$ ,  $\sigma_{C_{x'}H_{y'}^q}^{part}(E)$  the partial ionization cross section according to the process  $e + C_xH_y \rightarrow C_{x'}H_{y'}^q + \dots$ , and  $q$  denotes the charge state of the product ion, i.e. here  $q = +, 2+$ . Obviously,  $x' \leq x$  and  $y' \leq y$ . As the recent measurements have not been sensitive to distinguish fragmentation channels with respect to neutrals, the specification of the reaction channel with respect to product ions is sufficient.

For acetylene seven distinct reaction channels have been measured and data fits have been generated. Dividing these by the total ionization cross section, i.e. the sum of partial ones, seven branching ratios have been determined and compared to appropriate counterparts in HYDKIN. It is interesting to note that both, present branching ratios and those ob-



tained from HYDKIN clearly depart from energy invariance. Considering for instance the  $C_2^+, CH^+, C^+$  reaction channels the branching ratios appear to approach constant asymptotic values (if at all) only very slowly and far beyond  $10keV$ . In other cases, as the dominating  $C_2H_2^+, C_2H^+$  channels, the assumption of energy invariant branching ratios appears quite more reasonable, although only within certain limits. The branching ratio for the  $C_2H_2^{2+}$  yields, however, an absolutely different behaviour compared to the HYDKIN counterpart, increasing again actually beyond  $\sim 2keV$ . On balance, the typical energy dependence of branching ratios (with few exceptions as the parent ion channel) can be characterized by a sharp increase after the energy threshold, a broad maximum at  $20 - 200eV$  and a slow decrease afterwards.

In order to derive quantitative criteria for an approximation of constant branching ratios to be reasonable, the maximum deviations,  $\delta_{max}$ , from the mean values of the branching ratios,  $\langle R_j \rangle$ , have been calculated according to

$$\delta_{max} = \max \left( \left| 1 - \frac{\langle R_j \rangle}{R_j(E)} \right| \right), \quad (7a)$$

$$\langle R_j \rangle = \frac{1}{E_{max} - E_{min}} \int_{E_{min}}^{E_{max}} R_j(E) dE, \quad (7b)$$

where  $j$  indicates again the reaction channel,  $E_{max} = 10keV$ ,  $E_{min} = E_{th,max} + \Delta E \in (40, 60, 50)eV$  for  $(C_2H_2, C_2H_4, C_3H_6)$ , respectively. The latter has been chosen such that all reaction channels are open and considerable beyond the largest energy threshold to ensure a negligible influence of the energy threshold on the energy dependence of the branching ratio.

The two dominating  $C_2H_2^+, C_2H^+$  channels as well as the  $CH_2^+$  channel have smaller  $\delta_{max}$  ( $< 22\%$ ), where for the rest of the subdominant channels  $\delta_{max} = 30 - 50\%$ , with exception of the  $C_2H_2^{2+}$  channel with  $\delta_{max} = 315\%$ .

For the 13 distinct reaction channels in case of ethylene an analogous analysis of their branching ratios has been made. The branching ratios have mostly the typical behaviour as described above, with exception of the parent ion and the  $C_2H_3^+, C_2H_2^+$  reaction channels, where in the two latter cases the branching ratio decreases somewhat beyond maximum, but then increases again after reaching a local minimum at  $\sim 100eV$ . Considering the  $H_2^+, H^+$  reaction channels, one can again observe the unusual behaviour right beyond the energy threshold, which might be an indication that these cross sections are superpositions of cross sections referring to very different energy thresholds, see Sec. III B

Considering the maximum deviations from the mean,  $\delta_{max}$ , it has been observed that these are lower for the most dominant channels than for less dominant ones: The  $C_2H_4^+, C_2H_2^+$  channels have values of  $\delta_{max}$  even below 5% (together with the  $CH_3^+$  channel, however, being much smaller in magnitude), followed by the  $CH_2^+, C_2H_3^+$  channels with  $\delta_{max} = 12.8$  and  $\delta_{max} = 20.8$ , respectively. The rest of the maximum deviations are in a range of 37.9 – 66.8%. Separating reaction channels into dominant and subdominant ones, it appears that the assumption of energy invariant branching ratios would cause less failure (if the cross sections would be unknown and instead computed by applying scaling laws to known ones) in case of the dominant ones than in case of the subdominant ones. This is supported also by the analysis for acetylene, where the ionization is mostly dominated by only two reaction channels, namely the  $C_2H_2^+, C_2H^+$  channels, which add up to more than 90% of the total cross section at almost all energies. In view of underlying dissociation mechanisms, one might conclude that the dominating reaction channels are mainly given by dipole allowed transitions, whereas the stronger variation of the branching ratio with energy in case of subdominant reaction channels indicates greater involvement of alternative (non-dipole allowed) dissociation mechanisms.

Also interesting to note is the fact that the recent measurements for (dissociative) ionization of ethylene show a different ordering of contributing reaction channels with respect to the magnitude of the appropriate branching ratio compared to the ordering of cross sections given by HYDKIN. In the latter case the ordering is as follows, beginning with the largest contributing reaction channel:  $C_2H_4^+, C_2H_3^+, C_2H_2^+, C_2H^+, CH_3^+, CH_2^+, C_2^+, CH^+, C^+$ . Instead of this ordering the recent measurements yield the following:  $C_2H_4^+, C_2H_3^+, C_2H_2^+, C_2H^+, CH_2^+, CH^+, C^+, C_2^+, H^+, H_2^+, C_2H_3^{2+}, CH_3^+, C_2H^{2+}$ , where it has to be mentioned that the contribution of the  $C_2H_3^+$  channel actually becomes larger than that of the  $C_2H_4^+$  channel for energies beyond 1keV as well as the contribution of the  $CH_2^+$  channel becomes larger than that of the  $C_2H^+$  channel for energies beyond 200eV. Therefore, the ordering of contributing reaction channels to the total ionization cross section in case of ethylene is different compared to that one based on earlier data compiled by HYDKIN with respect to the following aspects:

- (a) According to the recent measurements there exist intersections between branching ratios for pairs of processes  $C_2H_4^+, C_2H_3^+$  and  $C_2H^+, CH_2^+$  in contrast to the partial cross section fits provided by HYDKIN, where the magnitude of the contribution

of the  $C_2H_3^+$  and  $CH_2^+$  channel to the total cross section is for all energies smaller than the contribution of the  $C_2H_4^+$  and  $C_2H^+$  channel, respectively. In addition are the contributions of the  $C_2H_4^+$ ,  $C_2H_3^+$  channels different by a factor of 1.5 – 2 in the case of HYDKIN, whereas they are approximately equal according to the recent measurements for energies larger than  $\sim 100\text{eV}$ .

- (b) The  $CH_3^+$  channel is on the fifth position in the HYDKIN ordering, whereas it appears next to the last in the present ordering. A small contribution appears reasonable also because of the molecular structure of ethylene ( $H_2C=CH_2$ ), because production of a  $CH_3^+$  ion gives rise to a rearrangement reaction chain like  $e + H_2C=CH_2 \rightarrow e + H:C-CH_3^* \rightarrow CH_3^+ + \dots$ .
- (c) The ordering of the subdominant  $C_2^+, CH^+, C^+$  channels according to HYDKIN, is  $CH^+, C^+, C_2^+$  according to the recent experiments.
- (d) For completeness it is noted that the present ordering includes also the  $H_2^+, H^+, C_2H_3^{2+}, C_2H^{2+}$  reaction channels, which have so far not been available in the HYDKIN database. It is also noted that the first three of them are larger than the  $CH_3^+$  channel (see (b)).

However, the ordering of the three most dominating reaction channels has been untouched below  $1\text{keV}$ , although their contribution to the total cross section is partitioned in another way. Noting that they add up to almost 90% of the total cross section, the changes of ordering and magnitude of the other channels are just small modifications on the scale of the total cross section.

An analogous analysis of the branching ratios for the 11 reaction channels, distinguished by product ions, measured for propene has been made. Beside the fact that the determined branching ratios for the  $C_2H_3^+, C_2H_2^+, C_2H^+, CH^+, C^+$  reaction channels have larger deviations from the mean of branching ratios (in a range of 35 – 154%), the six remaining channels (containing the dominating ones) have only a rather small deviation,  $\delta_{max} < 23\%$ . A smaller deviation from the mean of branching ratios has been found for the dominating reaction channels in cases of acetylene and ethylene and this holds also for the dominating reaction channels in the case of propene.

However, the magnitudes as well as the ordering of the branching ratios differ quite strongly

from those obtained from HYDKIN. Whereas the four most dominating reaction channels add up to about 80 – 90% of the total cross section, they do just for about half in HYDKIN. Many of the subdominant channels are therefore much smaller compared to their HYDKIN counterparts. The complete ordered set (beginning with the largest contribution) of contributing reaction channels given by HYDKIN [6] reads:  $C_3H_6^+$ ,  $C_3H_5^+$ ,  $C_3H_4^+$ ,  $C_3H_3^+$ ,  $C_2H_3^+$ ,  $C_2H_4^+$ ,  $C_2H_2^+$ ,  $CH_3^+$ ,  $C_2H_5^+$ ,  $C_3H_2^+$ ,  $CH_4^+$ ,  $CH_2^+$ ,  $CH^+$ , where the  $C_2H_4^+$ ,  $C_2H_2^+$  and the  $CH_3^+$ ,  $C_2H_5^+$  reaction channels interchange their positions for energies below 30eV and 70eV, respectively. In contrast, the complete ordered set (again beginning with the largest contribution) of contributing reaction channels obtained from the recent measurements reads:  $C_3H_5^+$ ,  $C_3H_6^+$ ,  $C_3H_3^+$ ,  $C_3H_4^+$ ,  $C_2H_3^+$ ,  $C_3H_2^+$ ,  $C_3H^+$ ,  $CH_3^+$ ,  $CH_2^+$ ,  $C_2H_2^+$ ,  $C_2H_4^+$ ,  $CH^+$ ,  $C^+$ ,  $C_2H^+$ , where the  $C_3H_6^+$ ,  $C_3H_3^+$  channels contribute almost equally to the total cross section, the  $C^+$ ,  $C_2H^+$  channels interchange their position for energies above  $\sim 2.5\text{keV}$ , and the  $C_3H_2^+$ ,  $C_3H^+$ ,  $C_2H_4^+$  channels have been added due to the peaks at  $m/z = 38, 37, 28$  Thompson, respectively, in the mass spectrum recorded at an electron energy of 100eV by Feil et al [10]. However, there have been reported no cross sections for these values of  $m/z$  and their contribution has been estimated to be  $\sim 10 - 20\%$  to the total cross section.

Comparison of these ordered sets and analysis of magnitudes of the branching ratios yields that the differences in magnitude and ordering of the contributing reaction channels to ionization of propene between present reaction channels and HYDKIN ones can be summarized in the following:

- (a) The ordering of the  $C_3H_y$ ,  $y \in \{3, 4, 5, 6\}$  (and most dominating) channels yields enhanced contribution for odd  $y$  compared to the HYDKIN ordering from  $y = 6$  counting straight down to  $y = 3$ . Indeed, the contribution of the  $C_3H_5^+$  channel is the largest, quite two times that of the  $C_3H_6^+$ ,  $C_3H_3^+$  channels (whose contribution is almost equal) and quite four times that of the  $C_3H_4^+$  channel. Together they add up to about 80 – 90% of the total ionization cross section of propene.
- (b) There exist  $C_2H_5^+$ ,  $CH_4^+$  channels in the ordered set of HYDKIN, which do not seem to have any non-negligible contribution to the total cross section at all according to the recent measurements.
- (c) Also the subdominant reaction channels differ as well in magnitude as in ordering.

## IV. CONCLUSION

Partial electron impact ionization cross sections have been analyzed for acetylene, ethylene and propene. Data fits are presented in analytic forms according to Eq. (1) and have been compared to earlier data compiled by the online cross section database HYDKIN.

For acetylene, rather good accordance is found in view of the dominating reaction channels, and larger deviations in case of sub dominating channels. One new cross section fit, i.e. one which has not been included in the database so far, for the  $(CH_2^+ + C^+)$  channel has been generated.

For ethylene, differences between the new cross section fits and the ones stored in HYDKIN have been rather small in case of dominating reaction channels, and have been larger for sub dominating ones. However, also in the case of dominating channels larger deviations have been observed at low energies (from threshold to maximum) reflecting a steeper increase of the cross sections right beyond the threshold. Five completely new cross section fits have been generated, which are those for the (sub dominating)  $(CH_2^+ + F^+)$ ,  $H_2^+$ ,  $H^+$ ,  $C_2H_3^{2+}$  and  $C_2H^{2+}$  channels.

The largest differences between present and earlier cross section fits have occurred in case of propene. While the parent ion channel does not deviate much from the counterpart in HYDKIN (within 34%), the  $C_3H_5^+$  and  $C_3H_3^+$  channels yield a totally different behaviour. While the former is actually the most dominating reaction channel, the latter is almost as large in magnitude as the parent ion channel. This reflects a totally different ordering of dominating reaction channels in the case of propene, which applies also to the sub dominating channels. Numerous new cross section fits without appropriate counterpart in the HYDKIN database have been generated, but lack in information of specified fragments.

The energy dependence of branching ratios has been investigated, and the (pre-)assumption of energy invariance has been found to be well based for dominating reaction channels within an accuracy of about 20%, and to be worse based for subdominating channels, where variations of branching ratios up to factors of 6 have been observed. Therefore, dipole allowed transitions remain the major underlying mechanisms for dissociative ionization of the three hydrocarbons under consideration, but especially for sub dominating reaction channels alternative non-dipole allowed transitions might have a more significant influence than expected from earlier data. This might be especially important when constructing cross sections for

which no experimental data exists. However, the pre-assumption of energy invariant branching ratios has proven to be at least sufficient to produce cross sections in the right order of magnitude.

On balance, it can be concluded that the differences between present data fits and earlier data summarized in HYDKIN cross sections may lead only to small modifications of the database, since the differences are rather small on the scale of total ionization cross sections. How sensitive simulations might be due to such small changes, could be shown by some sensitivity analysis proposed in Ref. [22], for which HYDKIN also provides the necessary tools.

This work shall be concluded with some general remarks. Firstly, the HYDKIN database as well as the analyzed experiments are based on hydrocarbons consisting of hydrogen, obviously dedicating their relevance to hydrogen plasmas. It remains questionable if such databases and results are applicable also to hydrocarbons consisting of hydrogen isotopes. Secondly, cross section experiments as well as calculations are done usually for room temperature. However, it has been shown that at least for the energy threshold of electron-impact ionization there exist both, temperature and isotope effects [23]. Since the energy threshold plays a crucial role for the energy behaviour of cross sections, also these two effects might lead to further modifications and corrections of the relevant databases for magnetic confinement fusion.

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- [1] U. Samm, Transactions of Fusion Science and Technology **53**, 223 (2008).
  - [2] V. Philipps, Phys. Scr. **T123**, 24 (2006)
  - [3] G. Federici, C.H. Skinner, J.N. Brooks, J.P. Coad, C. Grisolia, A.A. Haasz, A. Hassanein, V. Philipps, C.S. Pitcher, J. Roth, W.R. Wampler, and D.G. Whyte, Nucl. Fusion **41**, 1967 (2001)

- [4] R. K. Janev, and D. Reiter, *Phys. Plasmas* **11**, 780 (2004)
- [5] R. K. Janev, and D. Reiter, *Phys. Plasmas* **9**, 4071 (2002)
- [6] D. Reiter, and B. Küppers, <http://www.hydkin.de>, 2010
- [7] D. Reiter, and R. K. Janev, *Contrib. Plasma Phys.* **50**, 986 (2010)
- [8] S. Feil, K. Gluch, A. Bacher, S. Matt-Leubner, D. K. Böhme, P. Scheier, and T. D. Märk, *J. Chem. Phys.* **124**, 214 (2006)
- [9] N. Endstrasser, F. Zappa, A. Mauracher, A. Bacher, S. Feil, D. K. Böhme, P. Scheier, M. Probst, and T. D. Märk, *Int. J. Mass Spectrom.* **280**, 65 (2009)
- [10] S. Feil, A. Bacher, K. Gluch, S. Matt-Leubner, P. Scheier, and T. D. Märk, *Int. J. Mass Spectrom.* **253**, 122 (2006)
- [11] C. Tian, and C. R. Vidal, *J. Phys. B* **31**, 895 (1998)
- [12] C. E. Melton, *J. Chem. Phys.* **37**, 562 (1962)
- [13] B. L. Schram, M. J. van der Wiel, F. J. de Heer, and H. R. Moustafa, *J. Chem. Phys.* **44**, 49 (1966)
- [14] H. Nishimura, and H. Tawara, *J. Phys. B* **27**, 2063 (1994)
- [15] E. Illenberger, J. Momigny, in: *Gaseous Molecular Ions: An Introduction to Elementary Processes Induced by Ionization*, edited by H. Baumgärtel, E. U. Franck, W. Grünbein, *Topics in Physical Chemistry Vol. 2* (Steinkopff, Darmstadt; Springer, New York, 1992)
- [16] R. Loch, M. Davister, *Chem. Phys.* **195**, 443 (1995)
- [17] M. Davister, R. Loch, *Chem. Phys.* **191**, 333 (1995)
- [18] M. Davister, R. Loch, *Chem. Phys.* **189**, 805 (1994)
- [19] P. Plessis, P. Marmet, *Can. J. Phys.* **65**, 165 (1986)
- [20] NIST Chemistry WebBook, <http://webbook.nist.gov/chemistry>, 2010
- [21] S. Huber, Diploma Thesis, Innsbruck University, 2010
- [22] D. Reiter, B. Küppers, R. K. Janev, *Phys. Scr.* **T138**, (2009)
- [23] S. Matejčík, M. Stano, E. Vasekova, S. Denifl, J. D. Skalny, T. D. Märk, *Atom. Plasma-mater. Interac. Data Fusion* **14**, 12 (2008)